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Sediment-Water Partition Coefficients of Hydrophobic Persistent Organic Pollutants (POPs) for Different Sediments with Passive Sampler

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ABSTRACT: Partition coefficients of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined in sediments from five distinct contaminated sites in France (marine harbor, rivers canals and highway sedimentation tank). The assessment of the risk caused by such micropollutants requires, in most cases, the measurement of their availability. To access to this availability, low density polyethylene (LDPE) membrane samplers were exposed to these sediments under constant and low-level agitation for periods of 1, 2, 4, 7, 10, 14, 18, 22, 25, 29, 32, 39 and 46 days. Freely dissolved porewater contaminants concentrations were estimated from the concentration at equilibrium in the LDPE membrane. The depletion of contaminants in the sediments was monitored by the use of performance reference compounds (PRCs). Marked differences in freely dissolved PAH and PCB concentrations and resulting sediment- porewater partition coefficients between these five sediments were observed. Data set was tested onto different empirical and mechanistic models. As final findings, triple domain sorption (a total organic carbon, black carbon and oil phases model) could model PCB data successfully whereas the best fitting for PAH partitioning was obtained by Raoult's law model.

INTRODUCTION

Dredged contaminated sediment can often act as a sink for hydrophobic organic contaminants (HOCs) released into the surroundings environment. Strong sorption of nonpolar organic compounds to certain types of organic phase in sediments tends to reduce their potential of emission, their accessibility to microorganisms and their concentration in sediment porewaters (Cornelissen et al., 2005). This strong sorption, possibly to soot or char-like carbonaceous particles is responsible for the well documented failure of empirical relationships based on the fraction of organic carbon (f_{oc}) and organic carbon–water partition coefficients (K_{oc}) to correctly predict contaminant availability in sediments (Bucheli and Gustafsson, 2000). Furthermore, weathered mineral oil (MO) residues have been previously shown to exhibit sorption strengths of similar or even higher magnitudes as compared to black-carbon (BC), for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Cornelissen et al., 2005). Obviously, presence of soot and/or oil fractions in sediments may significantly limit HOC bioavailability and risks involved for the environment (Cornelissen et al., 2005).

Our study aims to determine the equilibrium state of these chemicals for 5 dredged sediments representative of different types of contamination sources. The estimation of

porewater concentrations (C_{pw}) of PAHs and PCBs were therefore determined by passive sampling experiments with low-density polyethylene (LDPE) strips exposed to the sediments in the laboratory. LDPE strips have been previously successfully used to assess freely dissolved concentrations of various HOCs in heavily contaminated harbor sediments (Allan et al., 2012). The depletion of the sediment by the passive samplers was monitored by the use of Performance Reference Compounds (PRC) (Brandt et al., 2012). Sediment- porewater partition coefficients, determined by combining these data with the total sediment concentration (C_{sed}), were then evaluated against various empirical and mechanistic partitioning models.

MATERIALS AND METHODS

Sediments Characteristics. The 5 dredged sediments were collected from contaminated sites across France and stored in 60 L barrels. All the sediment were selected to present contaminant concentrations higher than S1 threshold (for fluvial sediment) and N2 threshold (for marine sediment), according to French regulations on sediment dredging (Decree of August, 9, 2006). About 1200 kg (wet weight) of sediment were collected per site.

LDPE Membrane Preparation. Lay-flat LDPE tubing was purchased from Brentwood Plastics Inc. (St. Louis, USA) and reproducibly cut along the two edges resulting in 2.5 cm wide LDPE membranes (average membrane thickness of 80 μ m). 5 cm long membranes were pre-extracted twice with hexane, prior to the spiking with PRCs (Booij et al., 2002). The 10 PRCs were selected to cover a $\log K_{ow}$ range from 4.53 (anthracene-d10) to 7.3 (CB 204). Strips were kept at -20°C until further treatment.

LDPE Exposure in Sediment Slurries. Homogenized composites sub-samples were used for laboratory sediment exposition. Seventeen glass jars were filled with 350 g of wet sediment and one LDPE strip of 5 cm. These jars were covered with Teflon strip then capped with aluminium-lined lids and tumbled on a rotating system (5 rpm) over a period of 46 days at 20°C in the dark. LDPE strips were regularly sampled for kinetics study. Unexposed strips were also used as control samples over the exposure time period. C_{sed} and C_{pw} were both determined on the same samples.

Extraction and Analyses of LDPE Membranes and Sediment characterization. After exposure, strips were washed with milli-ro water and extracted twice by soaking overnight in hexane. Hexane extracts were combined and internal standards added. About 3 g of dry weight sediment sample were extracted using an accelerated solvent extractor (ASE 350, Dionex). Total organic carbon (TOC) concentrations were measured using a TOC-V analyzer (Shimadzu) coupled with a SSM-5000A. Black carbon was measured using the CTO375 chemothermal oxidation method (Bucheli and Gustafsson, 2000). Total hydrocarbons contents (THC) were determined using GC-FID (Autosystem XL, Perkin Elmer). PAHs and PCBs were analyzed by gas chromatography (Agilent 6850) coupled to tandem MS/MS mass spectrometer (Agilent 7000).

Overview of initial characterization of the 5 tested sediments is given in Table 1.

TABLE 1. Initial characterization of the 5 tested sediments including: black carbon (BC) and total organic carbon (TOC) content; contaminant concentration; total hydrocarbons content (THC) and texture.

	Unit	Evry	Dunkerque	Lens	Marseille	Nimy Blaton
Origin		HST*	Marine harbor	Canal	Marine harbor	Canal
BC - black carbon	%	0.00	0.06	0.66	0.22	0.35
TOC	%	3.20	2.85	13.9	4.93	10.6
Σ 14 HAP**	µg/kg	2550	7710	45700	37100	3360
Σ 7 PCB***	µg/kg	62.6	737	539	4050	312
THC (C10-C40)	mg/kg	4590	3170	9580	5340	6310
Texture		Sandy-silty	Silty-sandy	Clayey silt	Silty-sandy	Clayey silt

*highway sedimentation tank

** naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz[*a*]anthracene, benz[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenz[*a,h*]anthracene, benz[*g,h,i*]perylene

*** CB 28, CB 52, CB 101, CB 118, CB 138, CB 153, CB 180

Nonlinear and Linear Regression: Nonlinear and linear regressions were performed with Sigmaplot version 11 (Scientific Computing, USA).

RESULTS AND DISCUSSION

Contaminant Accumulation. A measurable accumulation for PAHs (14 among the 16 EPA) and PCBs (22 to 36 including the 7 indicator PCBs) into LDPE membranes was observed for all 5 sediments. Figure 1 presents the uptake curves obtained for 4 PAHs over the exposure time of 46 days. Accumulation process in the membrane obeys a first order kinetics for all the studied compounds and, as previously described (Huckins, 2006), the concentration in the membrane after a time t ($C_{LDPE}(t)$) is expressed in Equation 1:

$$C_{LDPE}(t) = C_{LDPE}^{eq} [1 - e^{(-k_e \cdot t)}] \quad (1)$$

where C_{LDPE}^{eq} (ng/g) is the concentration in the LDPE strip at equilibrium and k_e (d^{-1}) is the exchange rate constant. Data from recovery down to 85% and up to 115% were ruled out. PAH and PCB concentrations from control LDPE sampler were below limits of detection.

The uptake curves fit correctly with Equation 1 with significant coefficients of determination for all the contaminants. Triplicate analyses at day 14 and 46 show low relative standard deviation and good reproducibility (coefficient of variation between 1% and 9% for PAHs and 1% to 11% for PCBs). Most of the contaminants (92% and 96% of PAHs and PCBs respectively) had reached equilibrium state at 46 days. The exchange rates between LDPE strips and water were calculated from equation 1 for each contaminant.

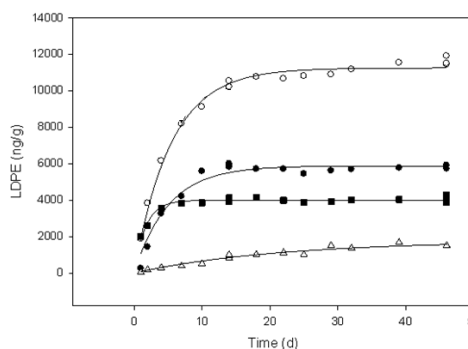


FIGURE 1. Accumulation of 4 PAHs (phenanthrene (■), pyrene (●), chrysene (○), benz [a]anthracene (△) in LDPE membrane exposed to Lens sediment.

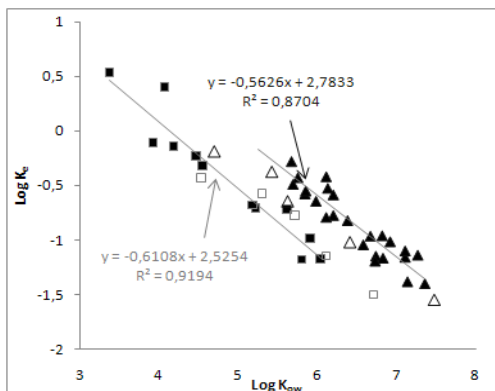


FIGURE 2. Exchange rate coefficients (k_e) as a function of $\log K_{ow}$ for passive sampling experiments with LDPE strips exposed to Lens sediment with PAHs (■), PAH-PRCs (□), PCBs (▲) and PCB-PRCs (△).

As shown in Figure 2, the estimated exchange rate constant k_e is well correlated to the hydrophobicity of the compounds represented here by the logarithm of the octanol-water partition coefficient ($\log K_{ow}$). The exchange rate constants for the added PRCs are in agreement with the values of the exchange rate constants observed for the native contaminants. Similar results were obtained by Booiij et al. (2003) and Allan et al. (2012) with LDPE strips exposed to harbors contaminated sediment. The slight difference observed for sorption equilibrium between both contaminant families could be explained, for identical $\log K_{ow}$, by higher exchange rate constant values for PCBs (Figure 2).

Moreover, as illustrated on Figure 3 for the PRCs, the exchange rates between LDPE strips and water differed for the five sediments tested despite the use of identical exposure conditions. This may be related to sediment properties such as particle size distribution, porosity, total organic carbon, black carbon and hydrocarbons content. Additionally, the level and origin of the contamination may influence the mass transfer into samplers.

Depletion Monitoring Using Performance Reference Compounds. Deducing pore-water concentration from this kind of experiments requires to check whether a non-depletive situation was really obtained, i.e., whether the sorption capacity of the sampler was well below that of the sediment. The depletion was monitored by the use of PRCs as proposed by Brand et al. (2012). A distribution factor (DF) corresponding to the ratio of the amount of PRCs remaining in the membrane and the amount of PRCs in the sediment at equilibrium was calculated for all the PRCs in each exposure conditions. When DF is 0.1 or less, the capacity of the coating is very small compared to that of the sediment. Consequently, the measured dissolved concentration in the porewater (C_{pw}) will not be affected significantly by depletion of analyte from the solid phase in the sediment. At the opposite, high DF values mean that there is little sorption capacity in the sediment and it is likely that the coating has taken a substantial fraction of the analyte from the solid phase of the sediment and therefore that the calculated

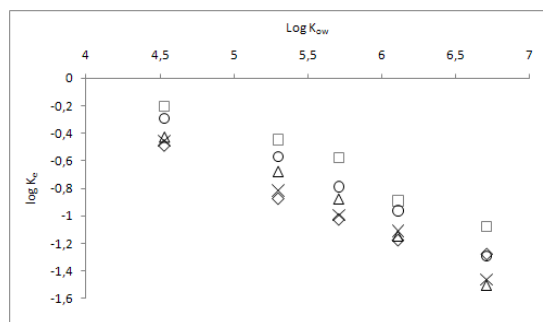


FIGURE 3. First-order dissipation rate constant ($\log K_e$) for PRCs spiked into LDPE membrane samplers exposed to Lens (△), Evry (□), Marseille (×), NB (◇) and Dunkerque (○) sediments.

C_{pw} value does not represent the original value. We calculated the DF values for all contaminants from experimental PRCs DF values. We decided to conserve data when equilibrium state was achieved and when the DF values was 0.1 or less for PAHs and 0.3 or less for PCBs. An underestimation of the porewater concentration by a maximum factor of 1.3 could be thus expected for PCBs. According to our consideration of acceptance or exclusion data, data of PAHs with $\log K_{ow} < 6.75$ were conserved for the five sediments whereas data of PCBs with $\log K_{ow} < 7.11$ were conserved for all sediments except for Evry. 62% of DF values for Evry sediment exceeded 0.3. This could be due to a poor concentration of native PCBs in the sediment and potentially related to a sandy structure with a low rate of condensed organic carbon phase (e.g., Table 1). Consequently, we only considered data of PCBs with $\log K_{ow}$ values below 6.38 for this sediment. Our measurement of different PRC dissipation rates for different sediments exposed under identical batch experimental conditions indicate the importance of the PRC use to confirm the equilibrium state and avoid an underestimation of C_{pw} .

Freely Dissolved Porewater Concentration. C_{pw} were then determined from LDPE concentrations at equilibrium fitted to Equation 1. For the present work, $\log K_{LDPE-water}$ for both PAHs and PCBs were calculated from the molecular weight (MW) according to Smedes et al. (2009) and considering, for PCBs, a specific term taking account of the chlorine position. The determined PAH dissolved concentration levels in porewater ranged from 0.146 ng/L for benzo[a]pyrene to 313 ng/L for pyrene. The dissolved concentration levels of PCBs were lower, ranging from 0.002 ng /L to 7.76 ng/L, respectively for CB 174 and CB 52. Higher PCB and PAH concentrations were observed, respectively for Marseille and Lens sediments.

Partition coefficients K_d and K_{TOC} . We compared our observations of sediment-porewater partitioning to equilibrium expectations based on sediment organic carbon content (f_{oc}), assuming the well documented relationship $K_d = f_{oc} \cdot K_{TOC}$. We used $\log K_{TOC,model}$ for PAHs and PCBs on the basis of the correlation with $\log K_{ow}$ established previously (Schwarzenbach et al., 2003). The $\log K_{d,exp}$ values observed were always higher than the theoretical values. The divergence of $\log K_{d,exp}$ values from such predictions was highest for PAHs than PCBs and exceeded on average $f_{oc} K_{TOC}$ products by about 1.5-1.9 log units. The $K_{d,exp}$ values for PCBs were higher than predicted by about 1 log unit. Absorption within organic carbon ($f_{oc} K_{TOC}$) is not sufficient to explain the sorption of native organic contaminants in these five sediments, as previously reported (Cornelissen et al., 2005). These results highlight the need to consider other sedimentary phases to account for the observed, stronger retention of the compounds investigated.

Nowadays, two kind of partitioning model are used in the literature: (1) mechanistic approaches mainly by accounting for the contribution of all sorbents, and (2) empirical approaches mainly by accounting for inner properties of each contaminants and sorption properties of one specific selected phase (coal tar, activated carbon) (Arp et al., 2009). For mechanistic approaches, the in situ distribution of POPs was evaluated using the double and triple sorption domain model (Equations 2 and 3).

$$K_d = C_s / C_{pw} = f_{oc} \cdot K_{TOC} + f_{BC} \cdot K_{BC} \cdot C_{pw}^{n-1} \quad (2)$$

$$K_d = f_{oc} \cdot K_{TOC} + f_{oil} \cdot K_{oil} + f_{BC} \cdot K_{BC} \cdot C_{pw}^{n-1} \quad (3)$$

in which K_d (L/kg) is the sediment- porewater distribution coefficient, C_s ($\mu\text{g/kg}$) and C_{pw} ($\mu\text{g/L}$) were the POP concentrations measured in sediment and water respectively, f_{oc} , f_{oil} , and f_{BC} were the measured organic matter, oil, and black carbon weight fractions (Table 1). K_{TOC} (L/kg), K_{oil} (L/kg), and K_{BC} ($[\mu\text{g/kg}]/[\mu\text{g/L}]$) were sorption constants for these respective phases. These latter partition coefficients were calculated from compound-class specific regressions with $\log K_{ow}$. Freundlich exponent (n) for nonlinear sorption to BC was set to 0.7 (Hawthorne et al., 2007).

Recent relationship published between ($\log K_{BC}$ or $\log K_{oil}$) and $\log K_{ow}$ are summarized in Table 2 (Equations 4 to 9). Experimental data from the 5 studied sediments were tested with double and triple domain sorption model, for the validation of the best combination among equation 4 to 9. Additionally, $\log K_{TOC}$ value were calculated according to Schwarzenbach et al. (2003).

TABLE 2. Relationships between K_{BC} , K_{oil} and K_{ow} for PAHs and PCBs.

Studied contaminant	Equation	Relationships f($\log K_{ow}$)	References
PAH	4	$\log K_{BC} = 1,6 \log K_{ow} - 1,4$	(Schwarzenbach et al., 2003)
PAH	5	$\log K_{BC} = 0,6997 * \log K_{ow} + 2,8219$	(Koelmans et al., 2006)
PAH	6	$\log K_{oil} = 0,2285 * \log K_{ow} + 5,9081$	(Jonker et al., 2003)
PCB	7	$\log K_{BC} = 0,912 * \log K_{ow} + 1,370$	(Werner et al., 2010)
PCB	8	$\log K_{BC} = 1,016 * \log K_{ow} + 0,2469$	(Koelmans et al., 2006)
PCB	9	$\log K_{oil} = 0,9948 * \log K_{ow} + 0,9787$	(Jonker and Barendregt, 2006)

For empirical approach, we tested the “coal tar model”, considered as the most appropriate polyparameter linear free-energy relationships (PP-LFER) based on the Abraham’s solvation parameters (Arp et al., 2009). Additionally, we also compared our set of data to the Raoult’s model, using coal tar as sorbent phase For PCBs, and for both models, we added a specific term based on abundance ratio of PCB congeners (WF), as a proxy for weathering, aiming for a better correlation (Hawthorne et al., 2011). WF is ranging from 0 to near 1, respectively for fresh to weathered contamination. From experimental concentrations of CB 28, 52 and 153, we obtained WF of 0.60, 0.75, 0.83, 0.86 and 0.96, respectively for Evry, NB, Lens, Dunkerque and Marseille sediments.

Models were considered successful for the prediction of average $\log K_d$ or $\log K_{TOC}$ when values were at 90% fitted within a difference of ± 1 log (factor ± 10) and at 99% fitted within a difference of ± 1.5 log (factor of ± 30) (Arp et al., 2009; Hawthorne et al., 2011).

For PAHs, among tested models, the best results were obtained for empirical models and particularly for Raoult’s law (Figure 4). This model predicts $\log K_{TOC}$ values in the differences intervals of ± 1 and ± 1.5 with frequencies of 91% and 100% of the values, respectively. The deviation on average is $-0.39 (\pm 0.52)$. Finally, Raoult’s law approach underestimates softly $\log K_{TOC}$ predicted. On the other hand, mechanistic model exhibited better results for PCBs (Eq. 3 with estimation of K_{BC} from Eq. 8 and K_{oil} from Eq. 9). Observed values were all included in the factors 10 and 30 confidence interval (Figure 4). This approach presented high level correlation with experimental values, the deviation on average was $0,05 \pm 0.32$ (factor of 1.1).

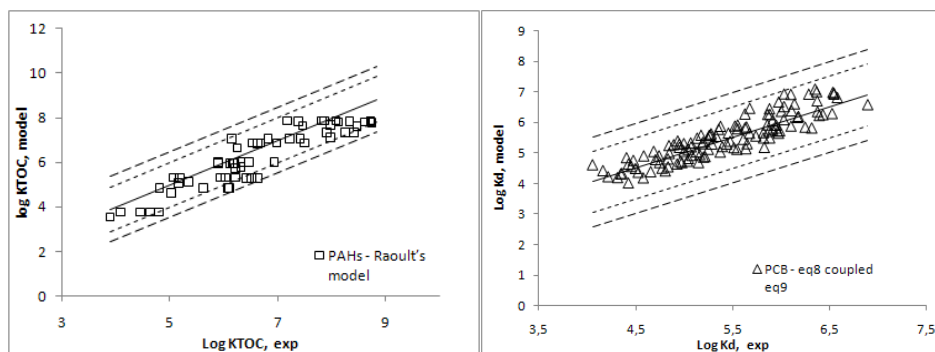


FIGURE 4. Representation of Raoult's law model for PAHs and triple sorption model for PCBs in studied sediments. The solid line is 1:1. The internal dashed lines represent the confidence interval suitable for a factor of 10 (1 log difference). The external dashed lines correspond to the confidence interval suitable for a factor of 30 (≈ 1.5 log difference).

CONCLUSION

Passive samplers with LDPE strips are suitable to measure porewater concentrations and thus to assess the sorption capacity (sediment/ porewater partition coefficient) of various contaminated sediments. Operational correlations between model predictions and experimental data were obtained for five distinct sediments. Predictive relationships for partitioning PAHs by mechanistic approach were proved to be insufficient. Best fit were obtained by Raoult's model using inner properties of each contaminant (water solubility) and coal tar sorbent phase concentration. For PCBs, triple domain sorption (a total organic carbon, black carbon and oil phases model) could model data successfully. The differences observed in PCB partitioning in the 5 sediments could be explained by the type and source of organic matter and source of the contaminants. Nevertheless, considering these two models, it should be kept in mind that 86% and 53% of the PCBs and PAHs respectively, fitted within a factor of 3. In term of contaminated sediment management, despite a good prediction for PCBs, the availability of contaminants should be assessed in most cases.

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